Block-Copolymer-Assisted Solubilization of Carbon Nanotubes and Exfoliation Monitoring Through Viscosity

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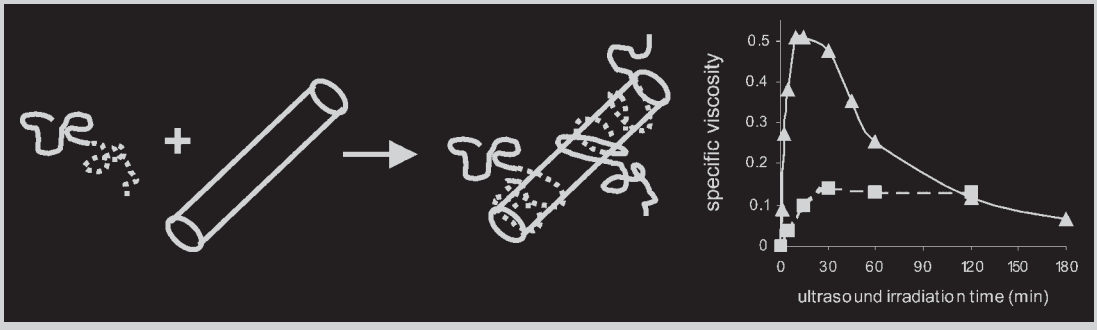
Summary: The use of the block copolymers polystyrene-*block*-poly(ethylene oxide) and poly(methyl methacrylate)-*block*-poly(ethylene oxide) is described to assist the direct solubilization of single-walled carbon nanotubes (SWNTs) into water under ultrasonic irradiation. As compared to surfactants and homopolymers, the block copolymer systems may offer the potential of additional unique morphologies through self-assembly. TEM and AFM analyses of solution-cast samples indicate exfoliation and wetting of the SWNTs by the block copolymer. With increasing duration of ultrasonic irradiation, an increase in solution viscosity is initially found, which suggests that it is a convenient indicator of the progress of exfoliation of the SWNTs. With increasing duration of ultrasonic irradiation, an increase in solution viscosity is initially found, which suggests that it is a convenient indicator of the progress of exfoliation of the SWNTs. With continued intense ultrasonic irradiation, the solution viscosity may decrease apparently because of damage/breakage of the SWNTs.



Schematic of the interaction of the PMMA-*b*-PEO block copolymer with the single-walled carbon nanotubes and the specific viscosity of the system in aqueous solution as a function of sonication time: results from using an ultrasound bath (----■----) or an ultrasound horn (—▲—).

Block-Copolymer-Assisted Solubilization of Carbon Nanotubes and Exfoliation Monitoring Through Viscosity

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Introduction

Enhancement of mechanical, thermal, electrical, barrier, and crystallization properties of polymers by composite formation with nanoparticles has been an area of intense research in recent years.[1,2] For this purpose, single-walled carbon nanotubes (SWNTs) are unique among nanoparticles because of their large aspect ratio, and mechanical as well as electronic and conductive properties.[3–8] For example, threshold concentrations of SWNTs in polymers for electrical conductivity have been reported to be as low as 0.015 wt.-%,[7] and the modulus and strength of nanocomposites with 1 wt.-% SWNTs are comparable with those of conventional fiber composites with 10 wt.-% carbon fibers.[8] Since the SWNTs tend to assemble into ropes of nanotubes, attainment of these properties in nanocomposites is largely dictated by exfoliation, uniform dispersion, and adhesion of the SWNTs with the matrix polymer.

The exfoliation is often achieved prior to mixing with the polymer, e.g., through covalent[9] or non-covalent[10] chemical modification of the SWNT surface. A convenient way of obtaining a stable SWNT dispersion is through sonification combined with interactions of nanotubes with macromolecules like poly(vinyl pyrrolidone) and poly(styrene sulfonate),[11] poly(metaphenylenevinylene) and derivatives,[12–15] poly[(vinylidene fluoride)-*co*-trifluroethylene],[16] amylose,[17] arabic gum,[18] gelatin,[19] block copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO),[20,21] and A–B–A-type block telomers.[22] Such solubilization is proposed to occur through wrapping of the polymers around the SWNTs[12,14,15,19,23] or via steric stabilizations.[17,21] Since only a limited number of macromolecules display the desired interaction with the SWNTs, low-molecular-weight surfactants[24,25] are often used to facilitate the good dispersion desired in polymeric nanocomposites. However, leaching/migration of the low-molecular-weight surfactants during use of the nanocomposites is a potential threat, and use of block copolymers can offer a relative advantage. Here, diblock copolymers of polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) and poly(methyl methacrylate)-*block*-poly(ethylene oxide) (PMMA- *b*-PEO) are employed. The observation of the solubilization behavior of SWNTs in water and toluene with these copolymers and constituent homopolymers indicates that the preferential interaction of one block (PS or PMMA) for the SWNTs and of the other block (PEO) for the solvent (water) leads to direct solubilization of the SWNTs in water under ultrasonication. However, the constituent homopolymers PS and PMMA are insoluble in water, and PEO is unable to stabilize the SWNT dispersion. In addition, it is shown that the increase of solution viscosity can emerge as a measure of the progress of exfoliation and solubilization with sonification. There is a clear need for such a technique to enable comparison of the effectiveness of various emerging methods of exfoliation, as a purely visual evaluation is not quantitative, and microscopy techniques for sufficiently (large) representative sampling[25] are rather demanding. It is further expected that an appropriately selected block copolymer will not only assist solubilization of SWNTs in a solvent, but will also improve subsequent dispersion and adhesion of the block-copolymer-modified SWNTs in an otherwise non-interacting polymeric matrix. More importantly, interaction of the self-assembling block copolymers with SWNTs of large aspect ratios may lead to unique new composite morphologies.

Experimental Part

The diblock copolymers PMMA-*b*-PEO and PS-*b*-PEO were used as obtained from Degussa Specialities/Th. Goldschmidt AG, Essen. For PS-*b*-PEO, the molecular weights of the PS and PEO blocks were 1 000 and 3 000, respectively. For PMMA-*b*-PEO, the molecular weight of each block was 1 000. The SWNTs were AP-grade and used as supplied by Carbolex, USA. They had an individual diameter of $\approx$1.4 nm, and lengths of $\approx$ 2–5 μm, and were made by the arc method as 'ropes' of $\approx$ 20 nm in diameter. The purity was 50–70 wt.-% and the impurities included approximately 35 wt.-% residual catalyst (Ni, Y), as well as some amorphous carbon.

Towards studying solvent viscosity development during ultrasonication, SWNTs (0.04 g) were suspended in water (20 mL) that contained PMMA-*b*-PEO (0.08 g) in a test tube. Such suspensions were subjected to ultrasonication for a desired time by either of the following two methods: i) the test tube was dipped into an ultrasound bath (Branson 2510, 42 kHz, 239 W) maintained at 60 °C, or ii) an ultrasound horn (13 mm, VibraCell Processor VC 750, operating at 40% of the maximum power of 750 W) was inserted into the test tube that was dipped in an oil bath maintained at 60 °C. The resulting solution was centrifuged for 15 min at 2 500 rpm (700 g), and the flow time of the supernatant solution was measured using an Ubbelohde viscometer (Schott Gerate 0c) at 30 °C. The specific viscosity was calculated by normalizing with the Ubbelohde viscometer flow time for a similar solution but without SWNTs. The effective SWNT concentration was 0.12%, while accounting for the $\approx$ 60% purity of the SWNT sample.

The nanostructure of the SWNTs with PS-*b*-PEO was characterized by transmission electron microscopy (TEM). One drop of a PS-*b*-PEO-stabilized SWNT (both 0.5 mg $\cdot$ mL^{-1}) solution in water was placed on a 400 mesh TEM grid and the water was allowed to evaporate in air. The sample was analyzed using a TEM Model JEOL 200FX with a bright-field at 80 kV accelerating voltage to increase the contrast.

Atomic force microscopy (AFM) was performed on a PMMA-*b*-PEO-stabilized SWNT (0.2 wt.-% of polymer and 0.5 mg $\cdot$ mL^{-1} of SWNTs) solution in water. One drop was placed on a silica substrate and the water was allowed to evaporate in air. The sample was analyzed using a MultiMode Scanning Probe Microscope (Nanoscope III) from Digital Instruments, Inc. (Santa Barbara, California) with NSG 11 'Golden' Silicon cantilevers (NT-MTD, Moscow, Russia), using a force constant of 11.5 N $\cdot$ m^{-1}.

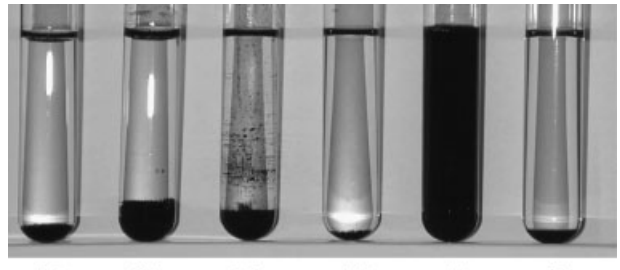

Figure 1. Observation of polymer-assisted SWNT dispersions in water/toluene after bath ultrasonication for 30 min. All tubes contain solvent (10 mL) with SWNTs (0.05 wt.-%) and polymer (0 or 0.2 wt.-%). Contents of the test tubes, from left to right: a) solvent: water, polymer: none, b) solvent: water, polymer: PEO, c) solvent: toluene, polymer: none, d) solvent: toluene, polymer: PS, e) solvent: water, polymer: PS-*b*-PEO, and f) solvent: toluene, polymer: PS-*b*-PEO. The images were taken two months after ultrasound application.

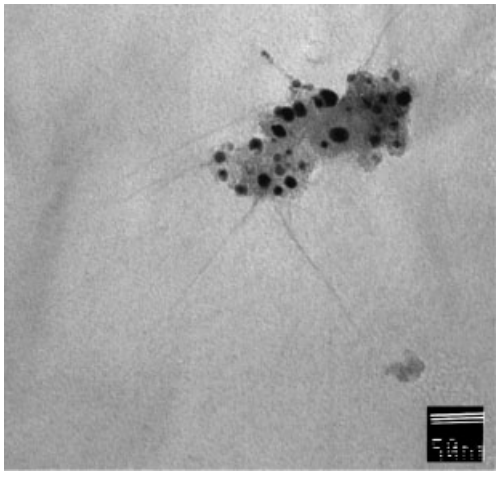

Figure 2. TEM image of an ultrasonicated SWNT/PS-*b*-PEO solution after water evaporation. The scale bar is 50 nm.

Results and Discussion

Figure 1 shows the polymer and ultrasound-assisted dispersion characteristics of SWNTs in two different solvents, toluene and water, which are good solvents for PS and PEO (blocks) respectively. Of the various shown trials, only the PS-*b*-PEO block copolymer is able to solubilize SWNTs, and only in water (Figure 1e). This indicates that the solubilization of SWNTs in water occurs by their physical association with the hydrophobic PS block, while the hydrophilic PEO blocks extend into the water and impart dispersibility to the SWNTs through steric stabilization.[18] Block copolymers are among the more efficient steric stabilizers because they are comprised of chemically distinct and often mutually incompatible moieties that are covalently bonded.[20] The block copolymer and the PS homopolymer are both unable to stabilize the SWNT dispersion in toluene (Figure 1f and 1d), which indicates that the strong PS/toluene association does not allow sufficient partitioning of PS onto the SWNT surface. The PEO homopolymer is unable to stabilize the SWNT dispersion in water (Figure 1b), and this indicates that PEO probably does not absorb on the SWNT from water. Similarly, PMMA-*b*-PEO is effective in solubilizing SWNTs in water, while the other combinations of the polymers (PMMA or PEO) and solvents (water or toluene) fail to solubilize the SWNTs.

Figure 2 shows the TEM image of the SWNT/PS-*b*-PEO dispersion dried on a TEM grid. It shows that during evaporation, dewetting of the grid surface occurs with the formation of islands of polymer, from which protrude the SWNTs (diameter $\approx$ 2 nm, Figure 2). Also seen in the image is a substantial amount of catalyst residue from the SWNT preparation. Figure 3 shows the tapping mode AFM of a SWNT/PMMA-*b*-PEO dispersion dried on a silica substrate. Again, it is possible to visualize some of the SWNTs. The height of the tubes is measured to be $\approx$ 1.2 nm, which corresponds to individual SWNTs. However, the measured diameter is higher, perhaps because of the broadening as a result of tip size or shape.

The high aspect ratio of the SWNTs leads to their solution rheology behavior being similar to that of rigid rod-like polymers that form liquid-crystalline phases.[26–29] This

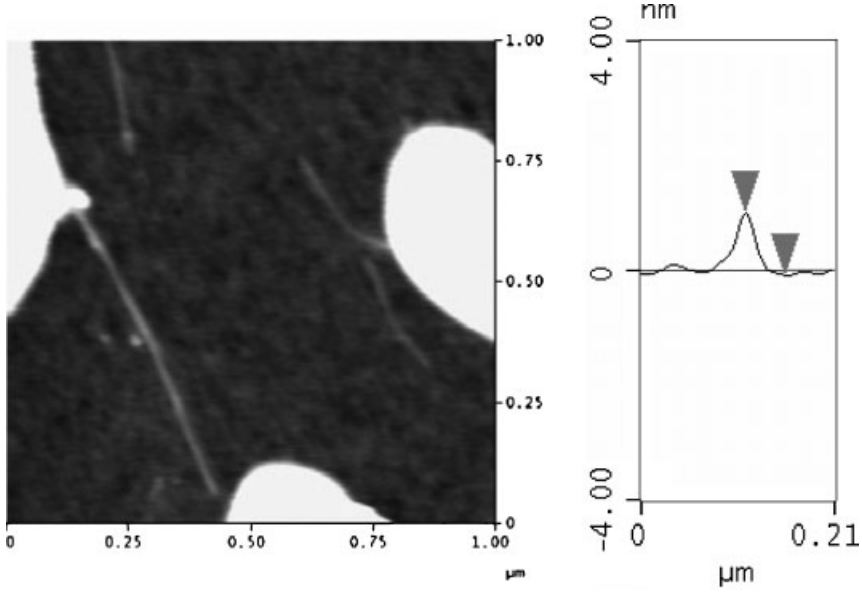

Figure 3. Tapping mode AFM height image of an ultrasonicated SWNT/PMMA-*b*-PEO solution after water evaporation.

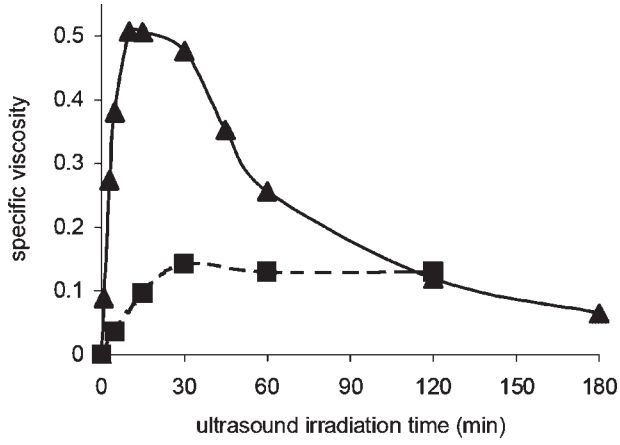

Figure 4. Specific viscosity of PMMA-*b*-PEO-based SWNT (0.4 and 0.2 wt.-%, respectively) solutions in water as a function of sonication time, using an ultrasound bath (----■----) or an ultrasound horn (—▲—). Repeat measurements of specific viscosity of a given solution varied from each other by less than 0.01. The viscosity of a solution of the low-molecular-weight copolymer alone was not affected by similar sonication.

suggests their possible use as rheology modifying additives. For example, rigid polymer molecules and fibrous particles have been shown to serve as drag reducing additives during turbulent flows.[30,31] Such behavior of large molecules is attributable to their large effect on solution rheology even at low concentrations. For example, a description of the steady shear flow of rod-like particles in solution leads to the viscosity (η_0) dependence on concentration (c), length (L), and diameter (D) of the particles shown in Equation (1) and (2):[32]

$$\eta_{sp} = \frac{\eta_o - \eta_s}{\eta_s} = \frac{8c(L/D)^2}{45\rho_b(\ln(L/D) - \gamma)} \quad \text{at} \quad v \ll 1/L^3 \tag{1}$$

$$\eta_{sp} = \frac{\eta_o - \eta_s}{\eta_s} \sim c^3(L/D)^6/\ln(L/D) \quad \text{at} \quad 1/L^3 < v < 1/DL^2 \tag{2}$$

where η_s is the solvent viscosity, η_{sp} is the specific viscosity, and v and ρ_b are the number concentration and bulk density of the rigid rods, and γ (= 0.8) is a constant. The high sensitivity of the solution viscosity η_0 to the rigid-rod parameters L and D suggests the possible use of solution viscosity (or η_{sp}) as an indicator of the progress of exfoliation of SWNT bundles during ultrasonic irradiation. The continuous curves in Figure 4 show the change in η_{sp} of aqueous dispersions of SWNTs and PMMA-*b*-PEO, with the time of ultrasonic irradiation with a horn.

Following Equation (1) and (2), the increase in η_{sp} from 0 to 0.5 in $t \approx 10$ min corresponds to an increase in L/D, which indicates exfoliation/dispersion. With continued irradiation from the ultrasound horn, η_{sp} decreases, and this is interpreted as a consequence of breakage/damage (and thus a possible decrease in average L) of the SWNTs. Measurements have also been carried out with milder ultrasonic irradiation by immersing a test tube containing the aqueous dispersion into an ultrasound bath, and the corresponding increase in η_{sp} is also shown in Figure 4 as a dotted line. It is found that the η_{sp} values here are lower than those obtained with the ultrasound horn, and indicate a smaller degree of exfoliation during the processing in the

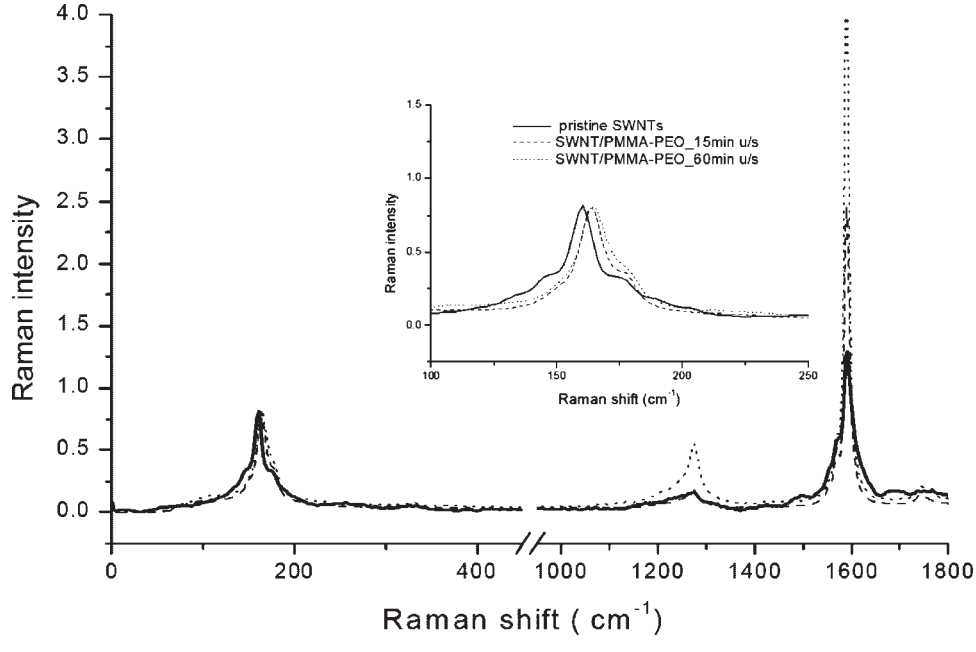

Figure 5. Raman spectra of a) pristine SWNTs, and of SWNT/PMMA-*b*-PEO dispersions after b) 15 min and c) 60 min of horn ultrasonication.

ultrasound bath. This suggests that even though uniform solubilization is easily achieved under mild sonification conditions (e.g., Figure 1e), the corresponding degree of exfoliation and possible damage/breakage has a strong dependence on at least the ultrasound intensity and irradiation time. For a chosen SWNT/solvent/surfactant system, it is expected that there is additional dependence on the concentrations of the SWNTs and the block copolymer, as well as on the temperature. The attainment of a maximum possible exfoliation with minimum damage/breakage, i.e., a maximum η_{sp}, requires optimization of the ultrasonic process. It appears that visual (Figure 1e) and microscopic examinations (Figure 2 and 3) are limited in their utility as indicators of SWNT exfoliation. Solution viscosity can be useful as a good and convenient measure of the progress of the exfoliation of SWNTs in solvent/surfactant systems.

These interpretations are supported by Raman spectra of the ultrasonicated solutions in the 100–250 cm^{-1} region (radial breathing mode, RBM).[33] As compared to the RBM peak at 160 cm^{-1} for the pristine SWNTs, the RBM peaks are located at ≈165 cm^{-1} for the dispersions after sonication. This suggests a reduction in the diameter of the SWNTs (and thus their exfoliation) with ultrasonication, since the RBM band frequency is inversely related to SWNT diameter. While the change in the RBM frequency is small for ultrasonication beyond 15 min, a large increase in the disorder peak at 1 278 cm^{-1} is seen for the sample ultrasonicated for 60 min (Figure 5). Since this is attributed to scattering from sp^3 carbon defects on the side walls of the SWNTs,[33] this supports the hypothesis that the decreasing dispersion viscosity on ultrasonication beyond 15 min (Figure 4) may correspond to damage to/breakage of the SWNTs.

Conclusion

Stable aqueous dispersions of SWNTs in water are achieved using amphiphilic diblock copolymers and ultrasonication. The increasing solution viscosity with time of ultrasonication suggests that the specific viscosity can be used as a simple technique to monitor the progress of the exfoliation. Intense and excessive sonication leads to a decrease in solution viscosity, which possibly indicates breakage of the SWNTs.

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